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ANALYTICAL

Report No. 100-100000

The intensely red waste waters from trinitrotoluene plants are among the most disagreeable waste waters of the chemical industry. As little as 1 mg of trinitrotoluene (TNT) per liter is fatal to fish. The toxicity of this explosive plant waste water is exceeded only by the waste water from hexanitrodiphenylamine plants, as little as 0.1 mg/liter of hexanitrodiphenylamine being lethal. There is hardly any useful method for detoxifying the TNT waste water, aside from evaporation followed by burning. Chlorination, admittedly, gives colorless waste water from TNT, but this method is inapplicable for economic reasons due to the high chlorine requirement of 3 g/liter. Precipitation with iron and aluminum is ineffective. Biological processes destroy the TNT, to be sure, but leave the coloring material intact. Treatments with activated charcoal, extraction methods (Phenosolvan), and acid adsorption precipitations on protein or nitrogen-containing plastics give only partial success. As these partial successes could be attained only with strongly acidic waste water, acid-resistant plants are necessary, making the process expensive. TNT waste waters have made many problems for plants, experimental laboratories, and river monitoring stations, and one can only hope that these waste water problems will always be a thing of the past. Therefore, we shall not consider the area of explosives waste water further, as great as its scientific interest is, and we shall consider only the acid economics of these waste waters to the extent that they may be of importance for waste water economics in other industries.

Construction of several TNT plants was started about the middle of the 1930's. Many factors were decisive in establishing the location: geographic, military, considerations of air defense and camouflage, aid for distressed areas, etc. These factories were also considered solely as preparedness plants, without a view to starting them up. Thus the plants appeared, in part, in the Harz and in the Hessian mountains, away from large rivers. Because of this, the waste water problem was not at all simple from the very beginning. When the requirements for quality and quantity of TNT later passed far beyond the original planning point, the waste water problems rose correspondingly. One of these plants produced up to 4,400 tons TNT per month in the last years of the war, although the planning had provided only for a peak capacity of 2,000 tons per month at considerably lower quality specifications. Merely for comparison, note that the entire German TNT production in the 1914/1918 period was only 3,000 tons/month.

The water usage of these plants was tremendous. Some 40,000 m³ water had to be used daily for the continuous production of about 4,000 tons of TNT per month. Most of this was cooling water, but 5-6,000 m³ of this considerable volume of water reappeared as acidic waste water contaminated with nitro compounds. Three varieties of waste water were of particular importance. They are characterized by the following details:

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Type of Waste Water	Manufacturing Wash Water	Condensate from sulfuric acid concentration	Building cleaning waste water
Volume: m ³ /hr	50	100	80
Appearance:	brick-red cloudy	almost colorless, clear	with great variations, almost clear and colorless to dark brown and slimy, even oily.
Acid content:	4 g/l H ₂ SO ₄ 2 g/l HNO ₃	2 g/l H ₂ SO ₄ 0.3 g/l SO ₂	5 g/l H ₂ SO ₄ 2 g/l HNO ₃ (highly variable)
Color of the waste water made weakly alkaline with lime and clarified:	deep dark red	light pink	dark red

To be sure, this great incidence of waste water cannot be considered as normal for 4,000 tons/month production. The fact that the plant had to produce more than planned increased the amount of waste water more than the increase in production, for various reasons. A plant initially dimensioned for 4,000 tons/month would have been more economical with waste water. In the last year of the war, there were also all the generally known problems with labor forces and raw materials. Plant mishaps sometimes took on grotesque forms. Several times, for instance, up to 15 tons of concentrated nitration waste acid flowed directly through the channel from the acid stores to the clearing basin. There, the severe evolution of nitrous fumes forced the staff into gas masks, proving very annoying.

Loosely covered open gutters are recommended as acid waste drains. Pipes of ordinary vitreous concrete require more than ordinary numbers of repairs because of the strong thermal stress (heat of dilution of the sulfuric acid). The bitumen preparations used for sealing bell and socket joints are not equal to these stresses, but Asplit, and especially El-Asplit, have proved good. Asplit is also to be preferred over bitumens because of its resistance to organic solvents. For instance, severe erosion at the bitumen seals can be observed with as little as 5 mg/l of toluene in the waste water. Lines of Mipolam have also proved good in some places.

The fact that the severely varying amounts of acid in the waste water must first be buffered in the compensating basins before any further processing requires no special comment. In order to be able to handle all accidents, four fore-basins of 600-1,000 m³ were built, even during the war, for each of the three waste waters. In each case, one of these basins was used as a compensating and clearing basin, while the other three were kept available as collecting basins. The size was quite sufficient for the requirements on these basins. In plants with little danger, where one need not plan on explosions, one reserve basin would suffice, along with one compensating basin.

Lime was used almost exclusively in the TNT plants to neutralize the waste water acid. The largest of these plants used 700 tons of it per month, on the average. Processing of calcium carbonate was limited to isolated cases because the carbonic acid evolved reduced the capacity of the clearing basins. Also, only the relatively cheap waste carbonate from industry could be used, because the sand content was a serious problem with the natural carbonates (crushed

limestone). On neutralization with calcium carbonate, the sulfurous acid remains in solution as calcium bisulfite, which can be oxidized by aeration in the presence of calcium bicarbonate. But the air oxidation of the condensate from the sulfuric acid concentration was unsatisfactory both in the laboratory and in the plant because the accompanying nitro-compounds have an inhibiting effect. This was also the cause for giving up carbonate neutralization of the condensate, which is the only process that would otherwise have been used, in favor of lime neutralization, where the sulfurous acid reappears in the clarification mud as CaSO_3 .

In large plants, the lime can be metered in conveniently only if it is added to the waste water as 5-10% lime milk. For a high lime requirement, the recommended starting material is high-percentage lump lime, as free of sand as possible, from which one prepares the current requirement for lime milk. Use of crushed lime is inadvisable, because slaking is unconditionally necessary, and this is difficult to control during continuous operation. With large consumption, pneumatic systems are necessary for technologically and hygienically satisfactory supply. These must be built for three transport routes (car-lime storage, lime storage-lime milk tank, car-lime milk tank). Such conveyor systems are also expensive in operation and maintenance, a viewpoint which can be of decisive significance with such worthless materials as waste water. Obviously, chutes, bucket conveyors, and similar systems are needed to convey lump lime, but these are cheaper and less sensitive in operation. Therefore, the use of slaked lime should be limited to a reserve of bagged lime kept ready for acid catastrophes. From the above, it is self-evident that the lime milk station should be placed so that a rail siding can be brought in conveniently.

It is desirable to design the lime milk station and the neutralization together. Where this cannot be realized, the lime milk must be conducted to the neutralization in a circulating main. This subjects the lime milk pumps to severe wear, from which not even thick-material circulating pumps can be protected. In our experience, large rotary plunger pumps have proved most reliable in operation for lime milk transport.

In designing the neutralization plant, it should be noted that the lime milk reacts relatively slowly with the acid. Thus, it is necessary to mix them continuously for several minutes. Where a difference in level can be utilized, this mixing can be attained conveniently and cheaply by cascades. Otherwise, turbostirrers or powerful recirculating blowers in the style of air-lift pumps must be provided. The course of neutralization can be monitored simply with test paper. More elegantly operating measuring electrodes with relay-controlled lime milk valves and recording equipment (pH recorder, conductivity indicator) offer inestimable advantages in monitoring operations of large plants.

Quite different forms of basins have proved good for clarifying the neutralized or weakly alkaline waste water. The clarified waste water contains all the nitric acid and a considerable portion of the sulfuric acid as calcium salts. With the tendency of gypsum to form supersaturated solutions, CaSO_4 concentrations up to 3.5 g/liter are not rare in the waste water.

As a large part of the lime flows away with the waste water as calcium nitrate and calcium sulfate, the insoluble contaminants in the lime milk, primarily CaCO_3 and sand, are enriched in the clarification mud. If the lime milk is utilized correctly by good control of the

neutralization, one can expect 70-80% gypsum in the dry clarification mud. Such high proportions cannot be attained with poorly burned carbonate-rich limes. To be sure, carbonate-rich muds can be pumped back for neutralization and reused, but they are loaded with gypsum carried along from the clearing basin. Recycling is worth while only if the proportion of gypsum in the dry mud has sunk below 20%. Pumps and lines wear seriously if there is marked sand content in the mud, so that, for this reason also, attention should be given to absence of sand in the lime milk.

The clarification muds contain some 98% water. Even with low water content, they are thixotropic and can be pumped large distances to sludge beds. Where the accompanying materials prevent bed-drying of the mud, as is the case, for instance, with the nitro compounds of the TNT waste water, which are strongly colored and which can be washed out, a special dewatering system must be installed. Rotary vacuum filters have proved good for this purpose. Dewatering to some 60% water can be attained with these filters. Dewatering tests with centrifugal apparatus have not been successful with the gypsum mud. If even the last traces of the accompanying organic materials must be removed, calcination of the mud may be considered. One of the TNT plants has done this for a long time in 20-meter rotary tube furnaces. With an appropriate excess of reducing agent (pan grinder gas and lignite dust) CaS can also be obtained. Unfortunately, only at acid contents above 50 g/liter does this product react with the waste water fast enough for it to be used for neutralization, with recovery of the sulfur as H_2S for sulfuric acid production.

The waste water treatment plants for the TNT factories were, therefore, no longer ordinary clarification systems, but regular plants. The largest of them required a continuous crew of 60 men. With more than 40 electric motors installed, it had a monthly power consumption of about 125,000 kWh.

In an average month, 700 tons of lime were processed (see Table). The operating costs were correspondingly high, some 35 Pfg. per m³ waste water. Furthermore, it was necessary to consider the water supply for communities further downstream. The neutralized waste waters, because of the organic contaminants still present, could not be discharged into the nearest drainage channels, but had to be pumped long distances to an inlet point below the endangered communities, so that special pumping costs increased the expenses even more.

The reasons which led to such unfavorable conditions in one case or the other were explained initially. The plants in question were continuously concerned with the waste water problem during the war. But when the first results which could be evaluated operationally became available, it was too late to realize them under the limited conditions of the war economy (lack of laborers, raw materials, technological materials and power).

With the various viewpoints which determine the location of a factory, any newly built plant can suddenly find itself in a similar situation, with difficulties of the greatest extent arising through the coincidence of several waste water problems which are in themselves insignificant. It will not always be possible to correct these problems satisfactorily and especially economically at a later time. In planning industrial plants, then, it is advisable to think the waste water problems through to the last consequence, and to treat them at equal importance with all the other problems in site selection.

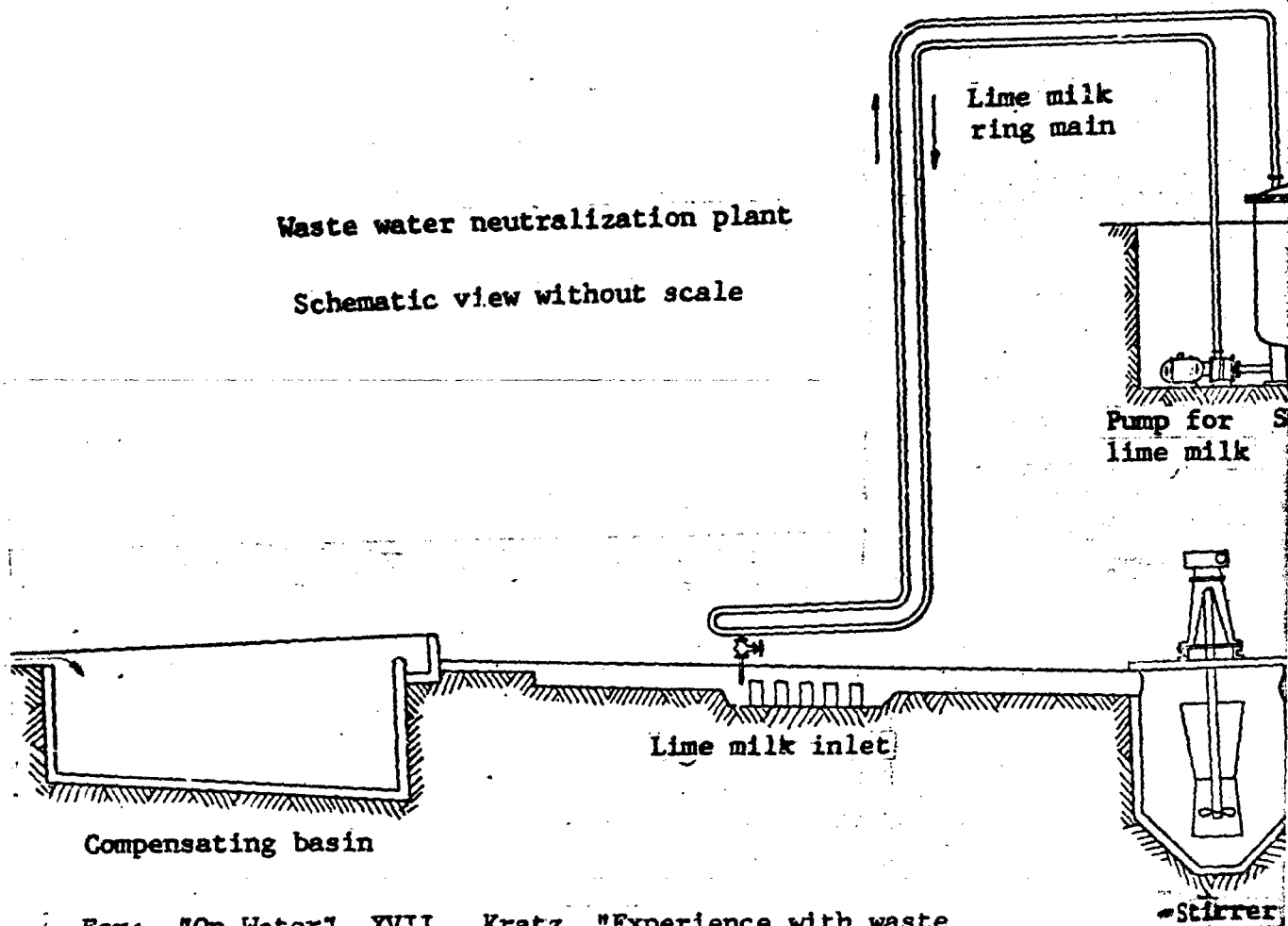
Editor's note: The extensive analytical documents were unfortunately lost to the author in March of 1945.

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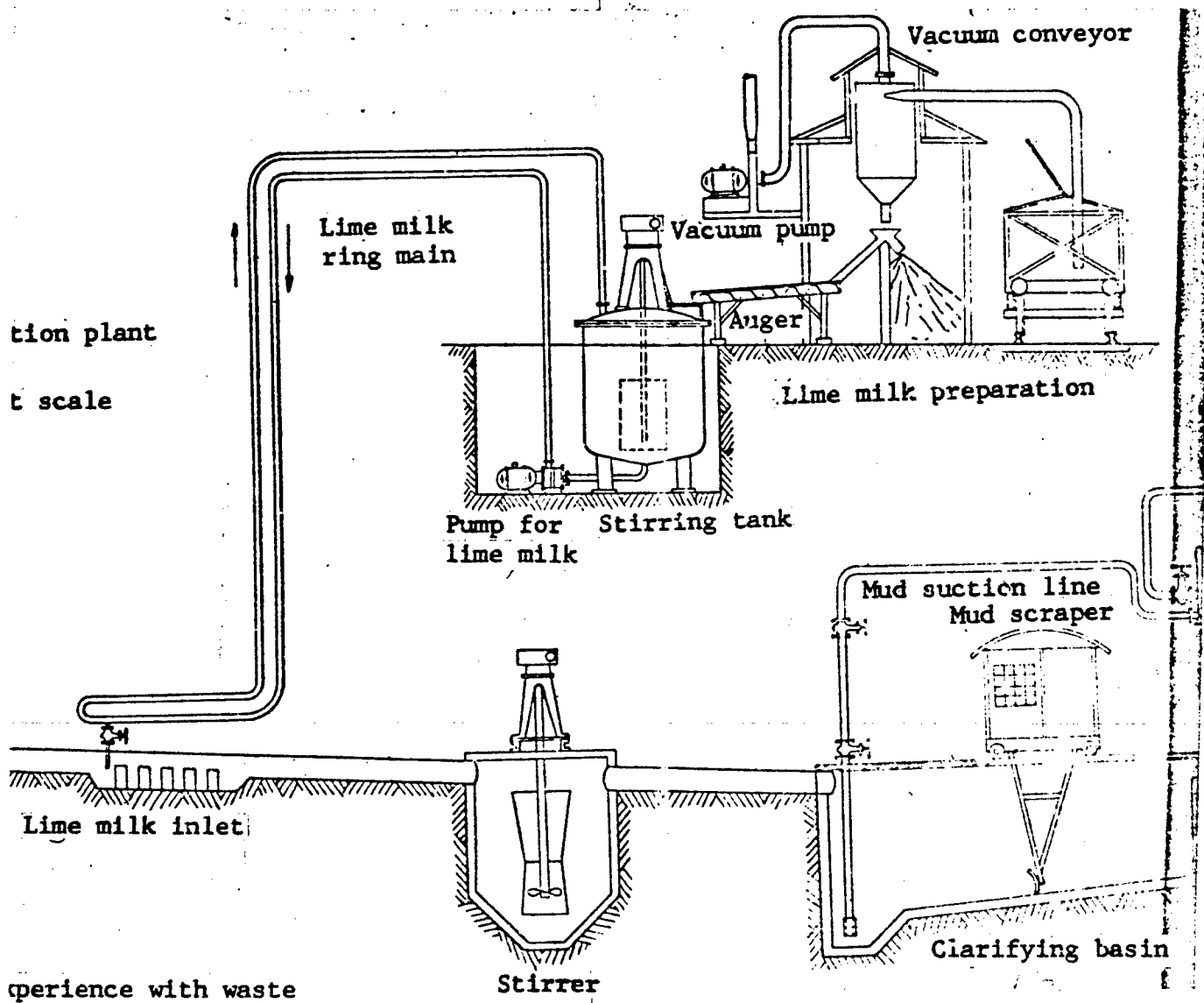
Waste water neutralization plant

Schematic view without scale



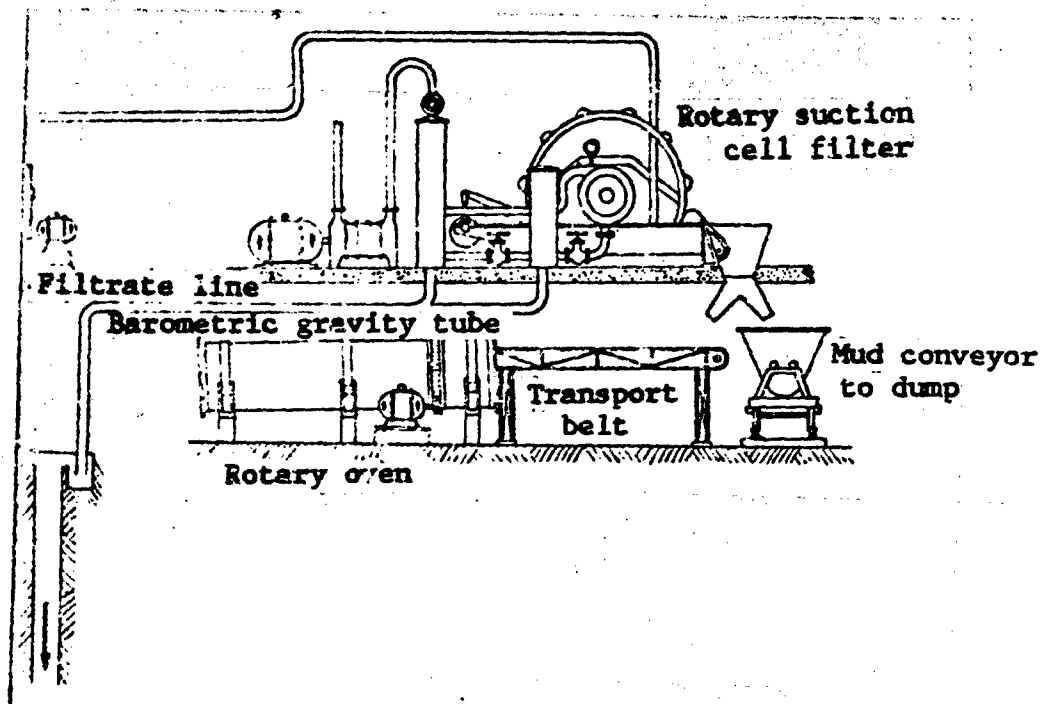
For: "On Water", XVII, Kratz, "Experience with waste water acid neutralization."

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